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Comparison of 0600-0900 AM Hydrocarbon Compositions Obtained from 29 Cities

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16. ABSTRACT

The report describes and compares 0600 - 0900 AM nonmethane organic carbon (NMOC) commpound data from 29 cities collected during summer periods of 1984 and 1985. Considerable differences are observed in those areas that are anticipated to have different volatile organic compound emissions. Range of benzene and toluene concentrations are presented for the 29 urban areas. It appears that variation in the observed concentration range is more evident for toluene than benzene. This observation suggests that there may be more discrete sources for toluene than benzene. The paper was presented at the 1986 EPA/APCA symposium on Measurement of Toxic Air Pollutants held in Raleigh, North Carolina during April 26-30, 1986 period.

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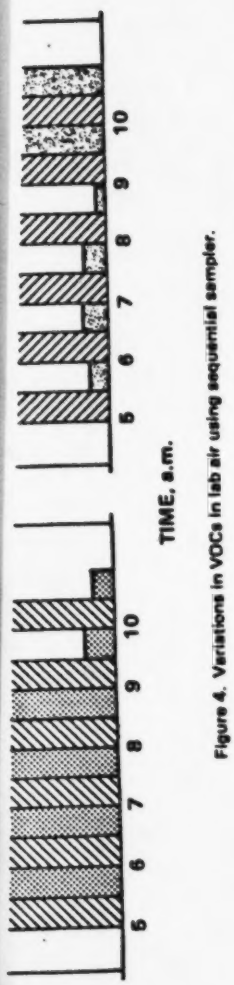

Figure 4. Variations in VOCs in lab air using sequential sampler.

COMPARISON OF 0600-0900 AM HYDROCARBON COMPOSITIONS OBTAINED FROM 29 CITIES

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Abstract

Mean nonmethane organic carbon (NMOC) compound concentrations are presented for 0600-0900 samples collected at 29 urban areas during the summer period of 1984 and 1985. Considerable differences are observed in those areas that have different volatile organic compound emissions. Ranges of benzene and toluene concentrations are presented for the 29 urban areas. It appears that variation in the observed concentration range is more evident for toluene than benzene. This observation suggests that there may be more discrete sources for toluene than benzene.

Introduction

A sampling program for nonmethane organic carbon (NMOC) compounds and the nitrogen oxides (NO_x) during the 0600 to 0900 period was conducted at several urban areas throughout the United States during 1984 and 1985. The purpose of the study was to obtain NMOC and NO_x information needed to prepare State Implementation Plans for ozone control strategies. Actually the cities participating in the study were identified in the Federal Register (1) as non-attainment areas for the National Ambient Air Quality Standard (NAAQS) for ozone. The 0600 to 0900 sampling period was selected to correspond with the guidance for the use of the Empirical Kinetic Modeling Approach (EKMA) for photochemical ozone control (2). According to the EKMA guidance, only 0600-0900 AM measurements of NMOC and NO_x are required at one representative central urban site location in the area to be modeled. There is also guidance for urban site location in terms of representing the general NMOC and NO_x emission patterns for the modeled area (3). Ideally, because of EKMA site selection requirements, the NMOC composition measured in the 29 urban sites reported here should represent all stationary and mobile sources in these areas.

NMOC determinations at the 29 urban sites were obtained from 3 hour integrated canister samples collected during the 0600-0900 AM period. The air sample canisters were shipped to a central laboratory facility located at Research Triangle Park, NC for total NMOC analysis using a cryogenic preconcentration FID approach (4). The measurement approach removed air and methane from the air sample permitting direct determination of NMOC. This approach was selected based upon the unreliable and inaccurate performance of continuous NMOC analyzers (5,6,7) typically used for these measurements.

Approximately 10 to 20% of the air samples were analyzed by detailed gas chromatographic procedures. Although the intent of the GC analyses was for quality assurance (QA) of the preconcentration total NMOC-FID approach, the detailed NMOC results are extremely useful for the evaluation and comparison of the NMOC compositions in these 29 urban areas located at diverse geographic areas of the United States. Some of the cities sampled have major industrial activities located within the urban area. Other cities have predominately vehicular NMOC emissions. Consequently large variation in NMOC compositions are expected among the 29 cities studied. Sampling during the 0600 to 0900 AM period provides only a limited period to compare NMOC composition. However, this time frame represents a period of active NMOC emissions and poor meteorological ventilation conditions. As a result, highest levels of NMOC concentration for these urban areas most likely occur during the 0600 to 0900 period.

The purpose of this paper is to compare NMOC compositions among the 29 cities to determine similarities and differences. Ranges for benzene and toluene are presented for the 29 sites since these compounds are under investigation as suspected toxic compounds.

Experimental

The sample collection device and analysis system used for the 1984 and 1985 studies have been published elsewhere (4). The publication contains detailed information concerning the sample canisters, the sample

collection device, the modified GC-FID system and the preconcentration procedure. Actually the preconcentration direct FID (PDFID) system described in this publication is similar to the ambient air GC-FID procedure without the GC column. The approximate 500 cc volume of ambient air trapped in the preconcentration system improves the sensitivity of FID system to measure ambient air NMOC concentration below 100 ppbC.

Details of the GC system (8) and the preconcentration procedure (9) have been published elsewhere. GC column conditions including flowrate and temperature programming conditions were identical for both the 1984 and 1985 studies. These conditions were unchanged between studies in order to directly compare 1984 and 1985 sample results. The column used was a 60 m x 0.32 mm i.d. DB-1 fused silica column (J & W Scientific, Cordova, CA). The helium carrier gas flowrate was maintained at 2-3 cm^3/min. The column temperature conditions consisted of an initial 1 min hold at -50°C followed by temperature programming at 8°C/min to a final temperature of 200°C with a final hold time of 5 min. Calibration of the individual compound peaks were performed with a National Bureau of Standards (NBS) 2.84 ppm propane in air Standards Reference Material (SRM) No. 1665b cylinder. A single response factor was used to determine all GC peak concentration. This approach has been determined to be valid for most hydrocarbon compounds (10). Canister samples were analyzed on the GC system generally within 2 to 4 days after collection.

At least one sample from each of the 29 urban areas was re-analyzed with chemical stripper columns (11, 12). A 4" x 1/2" stainless steel column packed with Ag_2SO_4 - H_2SO_4 on firebrick was used to remove all aromatic peaks except benzene which is approximately 60% removed. A 4" X 1/2" stainless steel column packed with $HgSO_4$ - H_2SO_4 on firebrick was used to remove all olefins peaks from the air sample.

Results and Discussion

The availability of detailed NMOC composition for 29 cities for the same calendar time period using the same GC analytical procedure is quite unique. In the past comparison of organic compositions in various cities consisted of using any available data collected over multi-year time periods determined by quite different GC analytical procedures. Such an approach can present serious problems when comparing complex chromatographic results such as those found in urban ambient air situations. This is particularly true for the comparison of the unidentified GC peaks observed in all chromatographic analyses of urban ambient air. The use of a single GC system, with air samples collected over a relatively short time span, presents a unique opportunity for the comparison of NMOC composition in these 29 cities. For the first time comparison among urban areas for unidentified compounds can be made with some reasonable degree of accuracy.

The 29 urban sites studies are listed in Table I. Those cities sampled in both 1984 and 1985 studies are identified with an asterisks to the left of the name. Eleven sites were sampled both years with 7 of these sites located in the State of Texas. The sites were assigned a different site number in the two studies. These site numbers are only important for following figures in which data results for the urban sites are unidentified by these numbers. As can be observed a large diversity of urban areas were sampled. These included cities with large industrial

sources, such as those in southeast Texas, to urban areas in which vehicular sources predominatee, such as Washington, DC and Boston, MA.

Two criteria were used to select samples for GC speciation analysis. First, the selected samples for all sites were equally distributed over the entire sampling period. An attempt was made to select an equivalent number of Monday, Tuesday, Wednesday, Thursday, and Friday samples to avoid possible day-of-week bias. Second, samples collected at sites that experienced afternoon ozone which exceeded 0.12 ppm were selected. It was anticipated that the GC analyses for high ozone days would be particularly useful to the States for their modeling studies. The latter criteria may result in a biased high average NMOC concentration for the GC samples at these sites since usually high precursor concentrations are observed on days of high afternoon photochemical ozone levels. However, NMOC emission patterns are expected to be somewhat consistent on a day to day basis. Consequently NMOC composition should not be significantly different on these high ozone days.

Figures 1 and 2 show a comparison of mean NMOC concentration by site for all samples analyzed with the PDFID procedure with those selected for detailed GC analysis. The general comparability between the two measurement procedures is quite reasonable for both the 1984 (Figure 1) and 1985 (Figure 2) studies. Perhaps the three sites demonstrating the most significant disagreement are site 1 (Akron, OH), Site 7 (Clute, TX) and site 14 (Miami, FL) all investigated during the 1984 study (Figure 1). The mean NMOC concentrations obtained by the GC procedure for sites 1 and 14 (Figure 1) are approximately 50% lower than the means measured by the PDFID procedure for all samples. The GC mean for site 7 (Clute, TX) is approximately 40% higher than that measured for all collected samples with the PDFID procedure. There appears to be little explanation for these significant variations. Samples were pre-selected by the same criteria as the other 19 sites. Also no samples were selected at these sites due to high ozone observations. Only three samples were analyzed by GC procedures at site 14 (Miami, FL) during the study period. Obviously the GC mean at that site is not representative of the NMOC mean concentration.

The comparison of GC with PDFID means for all sites sampled during the 1985 program (Figure 2) are much improved over the 1984 study. This is primarily due to the greater number of GC analyses performed at each site during 1985 program. The two sites that show significant disagreement are the Philadelphia sites 13 and 14. The GC means are approximately 25% higher than the PDFID means. For these two sites during the 1985 study pre-selection sample bias may be a legitimate explanation. Several samples were analyzed as the result of high afternoon ozone levels observed in the Philadelphia area.

Year to year comparisons of NMOC mean concentrations can be made for 11 sites common to both the 1984 and 1985 studies by reviewing the data in Figures 1 and 2. The only city showing a significant change was Beaumont, Texas. In 1985 the mean NMOC concentrate of 1.9 ppmC is nearly double the 1.0 ppm mean measured in 1984. None of the other 10 common sites

showed such significant changes. It is doubtful that meteorological changes over the one year period can explain such a significant increase. It is more likely that the NMOC emission levels were increased at the Beaumont site during 1985.

The number of GC peaks observed at the sites during both years ranged from about 100 on low NMOC concentration days to more than 240 peaks on the higher NMOC concentration days. Currently 65 of the GC peaks have been identified and verified by retention time location of pure hydrocarbon compounds. More than 175 peaks remain unidentified. In an effort to determine the nature of these peaks, collected samples were re-analyzed using stripper columns selective for the removal of olefin and aromatic compounds. Using this approach an assignment of the unidentified peaks as paraffinic, olefinic, and aromatic could be made. At least one pair of stripper column analyses were performed for each urban site studied during the 1984 and 1985 programs. No surprises were experienced with comparison of stripper column results from site to site. Each unidentified GC peak for all the urban site seemed to be the same type of hydrocarbon compound. Using the hydrocarbon classification assignments determined from the stripper column, total paraffin, olefin, and aromatic percent compositions were determined for each site. These percents of hydrocarbon compositions are shown in Figures 3 and 4.

In both Figures 3 and 4, it is apparent that paraffins are the most abundant species of hydrocarbon at all sites ranging from 50 to 60% of the total NMOC. Aromatic hydrocarbons are typically the next most abundant hydrocarbon type ranging from 20 to 30% of total NMOC. Olefins are the least abundant class of hydrocarbon observed ranging from 15 to 20% of total NMOC. This general composition breakdown, however, is not observed at the industrial-urban sites located on the southeast coast of Texas. At site 7 (Clute, TX) during the 1984 study (Figure 3) tne percent olefin level was higher than percent aromatic. Similar observations were made for Clute (Site 5) during the 1985 study (Figure 4). Site 1 (Beaumont, TX) showed a more abundant level of olefin than aromatic composition during the 1985 study (Figure 4). In both the 1984 study (Figure 3) and the 1985 study (Figure 4) equally abundant levels of olefins and aromatics were observed at the Orange, TX and Texas City, TX sites. It is obvious that the petrochemical industries in these areas have a significant impact on the NMOC composition. The hydrocarbon composition in the urban areas investigated in both studies appear to be quite similar. This is not surprising since vehicular sources are expected to comprise the largest percentage of NMOC emissions in these areas.

The availability of detailed hydrocarbon compositional information for these 29 urban areas provides a wealth of information to compare NMOC emission sources affecting these areas. Mobile and industrial sources typically have fingerprints or hydrocarbon patterns that discriminate the NMOC composition. Also the availability of individual species information enables one to compare concentration levels in these different areas. This is particularly important when these individual NMOC compounds are suspected as toxic pollutants such as benzene and toluene.

In Figures 5 and 6 are plotted mean, median, high and low concentrations for benzene and toluene observed during the 1984 study. In Figure 5 the range between high and low concentrations are not very large and are

perhaps the result of meteorological differences between these two sample days. Consequently the sources of benzene are suggested to be relatively consistent during the 0600-0900 AM period. The ranges between high and low at site 3 (Birmingham, AL), site 6 (Chattanooga, TN), and site 12 (Indianapolis, IN) are quite different and suggest that large discrete benzene sources affect these sites. These periodic high values significantly affect the mean concentration. This is observed by the comparison of the mean with the median concentration. In Figure 6 large ranges between high and low concentration are observed at more sites for toluene. This would suggest that there are discrete sources of toluene periodically affecting more of the urban areas. This is not unexpected since toluene is a very common organic compound used as a solvent and in many manufacturing processes.

Similar benzene and toluene observations can be made for the 1985 study (Figures 7 and 8). Again the range between high and low concentration at several sites is perhaps a result of meteorological variations. Periodic discrete sources of benzene are most evident at site 1 (Beaumont, TX), Site 17 (St. Louis, MO), and Site 18 (Texas City, TX). Again, more discrete periodic sources of toluene are evident in the range of high and low concentrations (Figure 8).

Conclusion and Summary

The availability of detailed hydrocarbon compositional information for 29 urban areas sampled during the 0600-0900 AM period for two summer periods and analyzed on one detailed GC system is unique. This data base allows one to compare NMOC composition for a variety of urban areas that have significantly different NMOC emission source patterns. Using one GC system allows the comparison of unidentified compound peaks between cities. In 1986 an additional 7 cities will be added to the list of 29. These cities include Denver, CO, Salt Lake City, UT, New York City, Chicago, Hartford, CT, Bridgeport, CT, and Tulsa, OK. Consequently these comparisons will be even more extensive.

REFERENCES

1. Federal Register, Vol. 48, February 3, 1983, p. 4972.

2. U.S. Environmental Protection Agency, Guideline For Use of City Specific EKMA in Preparing Ozone SIPS, Research Triangle Park, NC, EPA-450/4-80-027, (1981).

3. U.S. Environmental Protection Agency, Guidance for Collection of Ambient Non-Methane Organic Compound (NMOC) Data for Use in 1982 Ozone SIP Development and Network Design and Siting Criteria for the NMOC and NO, Monitors, Research Triangle Park, NC, EPA 450/4-80-011, (1980).

4. U.S. Environmental Protection Agency, A Cryogenic Preconcentration-Direct FID (PDFID) Method for Measurement of NMOC in Ambient Air, Research Triangle Park, NC, EPA 600/4-85-063, (1985).

5. F. McElroy and V. Thompson, "Hydrocarbon Measurement Discrepancies Among Various Analyzers Using Flame Ionization Detectors," U. S. Environmental Protection Agency, Research Triangle Park, NC, EPA-600/4-75-010, (1975).

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of NMOC in Ambient Air,
063, (1985).

Measurement Discrepancies
ation Detectors," U. S.
n Triangle Park, NC,

6. J. W. Harrison, M. L. Timmons, R. B. Denyszyn, C. F. Decker, "Evaluation of the EPA Reference Method for the Measurement of Non-methane Hydrocarbons," U. S. Envvironmental Protection Agency, Research Triangle Park, NC, EPA-600/4-77-033, (1977).

7. H. G. Richter, "Analysis of Organic Compound Data Gathered During 1980 in Northeastern Corridor Cities," U.S. Environmental Protection Agency, Research Triangle Park, NC, EPA-450/4-83-017, (1983).

8. F. F. McElroy, V. L. Thompson, D. M. Holland, W. A. Lonneman, and R. L. Seila, "Cryogenic Preconcentration-Direct FID Method for Measurement of NMOC: Refinement and Comparison with GC Speciation," JAPCA, in Press.

9. W. A. Lonneman, "Ozone and Hydrocarbon Measurement in Recent Oxidant Transport Studies," Proceedings of the International Conference on Photochemical Oxidant Pollution and Its Control, U. S. Environmental Protection Agency, Research Triangle Park, NC, EPA-600/3-77-001a, p. 211-223, (1977).

10. W. A. Dietz, "Response Factor for Gas Chromatographic Analyses", J. Gas Chromatog., 5, p. 68-71, (1967).

11. D. L. Klosterman, J. E. Sigsby, "Application of Substractive Techniques to the Analyses of Automotive Exhaust," Environ. Sci. Technol., 1, p. 309-314, (1967).

12. W. A. Lonneman, J. J. Bufalini, R. L. Seila, and R. L. Kuntz, "Subtractive Techniques for Analyzing Natural Olefinic Hydrocarbon," J. Environ. Sci. Health, A18(4), p. 527-538, (1983).

Table I. Urban Sites Sampled for Detailed NMOC Measurements During the 1984 and 1985 Studies

Site ID	1984 Site Number	1985 Site Number
Akron, OH	1	--
Atlanta, GA	2	--
Birmingham, AL	3	--
* Beaumont, TX	4	1
Boston, MA	--	2
Baton Rouge, LA	--	3
Charlotte, NC	5	--
Chattanooga, TN	6	--
Cincinnati, OH	8	--
Cleveland, OH	--	4
* Clute, TX	7	5
* Dallas, TX	9	6
* El Paso, TX	10	7
* Fort Worth, TX	11	8
Houston, TX	--	9
Indianapolis, IN	12	--
* Kansas City, MO	13	10
Lake Charles, LA	--	11
Miami, FL	14	--
Memphis, TN	15	--
* Orange, TX	16	12
* Philadelphia, PA (1)	17	13
Philadelphia, PA (2)	--	14
Portland, ME	--	15
* Richmond, VA	18	16
St. Louis, MO	--	17
* Texas City, TX	19	18
Wilkes-Barre, PA	20	--
* Washington, DC	21	19
West Palm Beach, FL	22	--

*Sampled in both 1984 and 1985 studies

Average Mean NMOC Concentration ppbC

Figure

Average Mean Concentration ppbC

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Figure 2

Measurements During the

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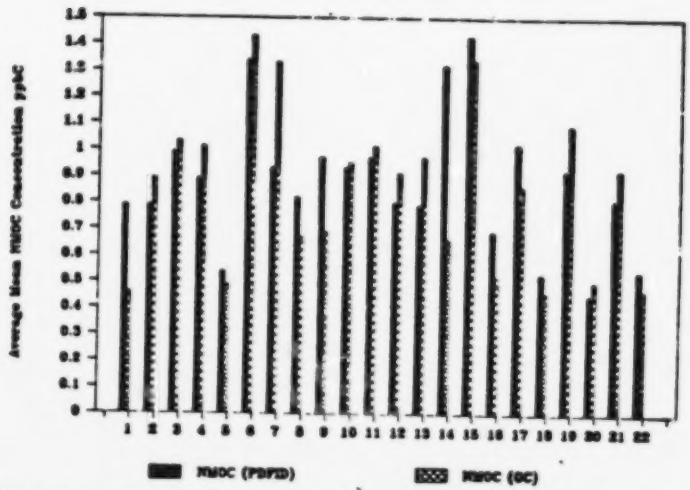


Figure 1. Comparison of average mean concentrations obtained with the PDFID and GC procedures for cities participating in the 1984 twenty-two cities NMOC study.

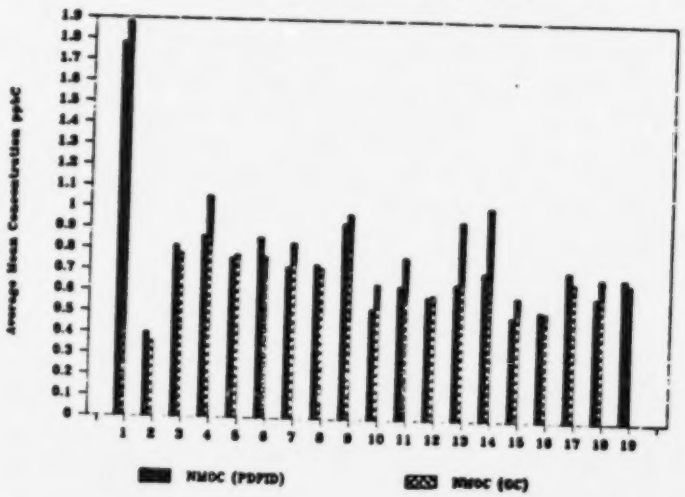


Figure 2. Comparison of average mean concentration obtained with the PDFID and GC procedures for cities participating in the 1985 nineteen cities NMOC study.

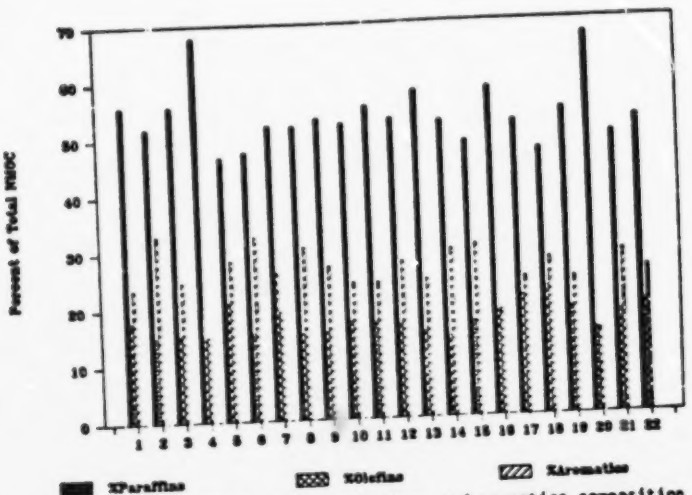


Figure 3. Percentage paraffins, olefins, and aromatics composition for the cities participating in the 1984 twenty-two cities NMOC study.

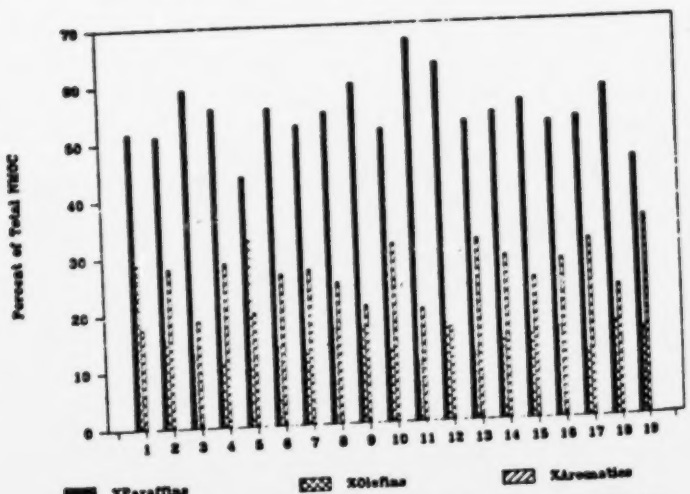
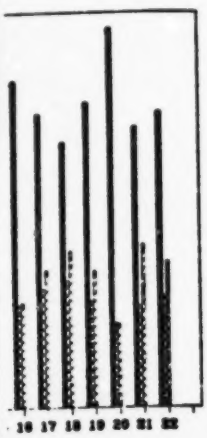


Figure 4. Percentage paraffins, olefins, and aromatics composition for the cities participating in the 1985 nineteen cities NMOC study.



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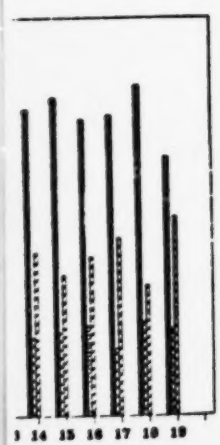

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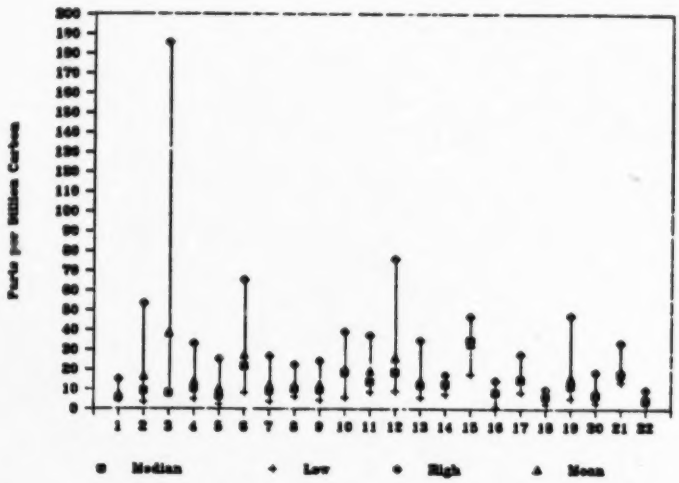

Figure 5. Mean, median, high and low concentrations of benzene observed at each city participating in the 1984 twenty-two cities NMOC study.

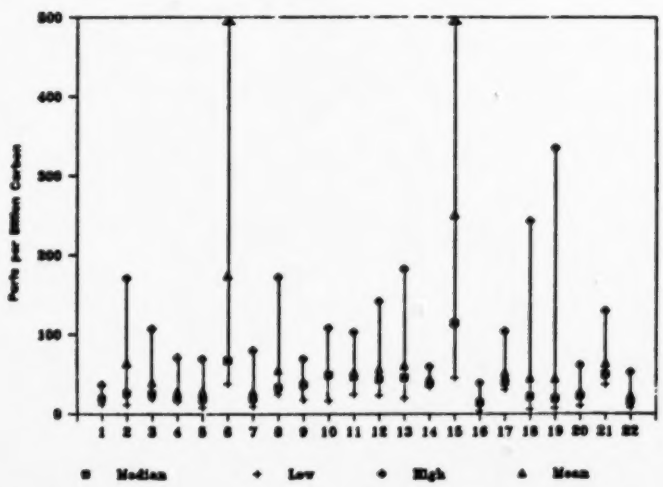

Figure 6. Mean, median, high and low concentrations of toluene observed at each city participating in the 1984 twenty-two cities NMOC study.

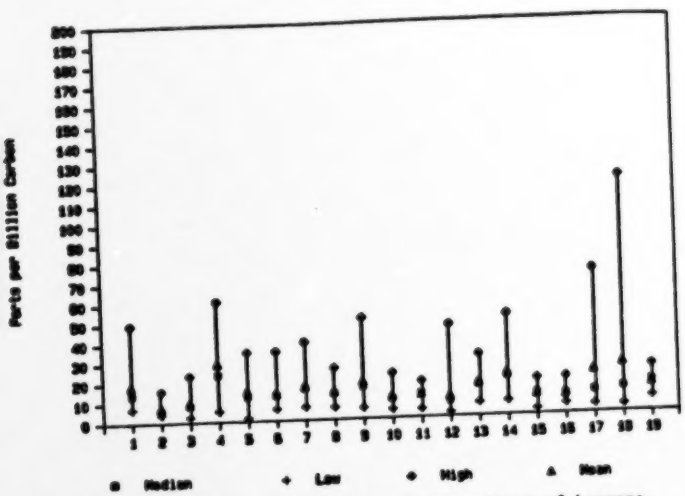

Figure 7. Mean, median, high and low concentrations of benzene observed at each city participating in the 1985 nineteen cities NMOC study.

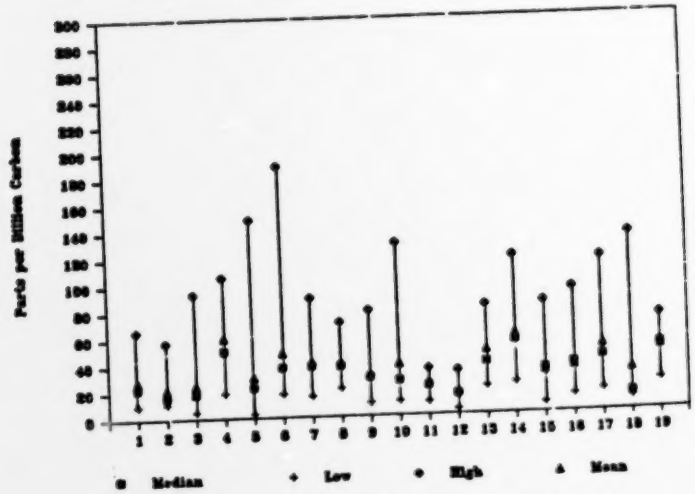

Figure 8. Mean, median, high and low concentrations of toluene observed at each city participating in the 1985 nineteen cities NMOC study.